

PATENT SPECIFICATION

NO DRAWINGS

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885,521

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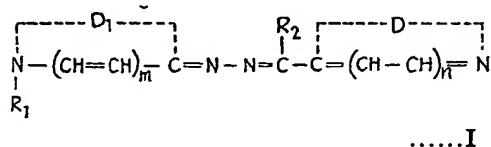
COMPLETE SPECIFICATION

Diazacarbocyanines

We, J. R. GEIGY S.A., a Swiss Company of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new diazacarbo-cyanine dyes.

In our co-pending Application No. 20414/58 (Serial No. 885,520) there is described *inter alia*, a new class of diazacarbo-cyanine bases of the general formula I:—



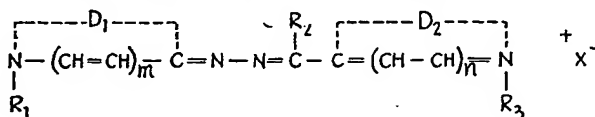
wherein R_1 is an alkyl or aralkyl group, R_2 is an alkyl, aryl or aralkyl group, m and n are the same or different and are each nought or one, and D_1 and D_2 are the same or different and are each a residue of a five-membered or six-membered heterocyclic nitrogen nucleus.

It is to be understood that the heterocyclic nuclei may be polynuclear, the additional rings being themselves isocyclic. Thus each may contain a fused benzene ring as, for example, in a quinoline nucleus. Phenyl groups and fused isocyclic groups present in the compounds may themselves carry substituent groupings, e.g. alkyl, aryl, alkoxy, hydroxy, amino or acyl-amino groups or halogen atoms (e.g. chlorine or bromine).

Examples of heterocyclic nuclei of which D_1 and D_2 may be the residue are thiazole, pyridine, pyrimidine, thiadiazole and their partially reduced derivatives (e.g. thiazoline) and the polynuclear derivatives of these such as benzothiazole, quinoline and benziminazole. Where the residues D_1 and D_2 include tertiary nitrogen atoms of the form $-\text{NR}^1-$, R^1 may be hydrogen, alkyl, aryl or aralkyl.

The group R_1 may be an alkyl group containing up to 4 carbon atoms and the group R_2 may be an alkyl group containing up to 4 carbon atoms or a phenyl group.

According to the present invention there are provided quaternary cyclammonium salts of the said compounds of formula I, being compounds of the general formula II:—



where the symbols R_1 , R_2 , D_1 , D_2 , m and n have the meanings assigned to them above, R_3 is an alkyl or aralkyl group and X is an anion, e.g. toluene-*p*-sulphonate, halide (chloride, bromide or iodide), sulphate, methosulphate, perchlorate or sulphamate.

Preferably the said compounds are pre-

pared by treating a compound of general formula I with a quaternising agent of the formula R_3X , e.g. by refluxing with or without an inert solvent, if R_3X is of suitable volatility, or by fusing the reactants at elevated temperature.

The resulting dyes are valuable dyestuffs for

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polymeric materials consisting essentially of polymers of acrylonitrile and copolymers of acrylonitrile with other monomeric materials. Generally the polymers will contain at least 85 per cent of acrylonitrile units and a particular commercial material of the type, essentially in the form of textile fabric, is sold under the Registered Trade Mark ORLON. Such polymers are difficult to dye by the use of conventional dyestuffs and the compounds of the present invention provide a new class of dyestuff of exceptional value in the dyeing of such materials. The dyeing is preferably effected in a dilute acid medium or in a dispersion.

The dyes of formula II may be rendered of suitable solubility by treating with an aqueous solution of a salt MY where M is ammonium or an atom of an alkali metal (e.g. sodium or potassium) and Y is an anion, e.g. any of those referred to in connection with X whereby the radicle X is replaced by the radicle Y so that the solubility of the product is varied. Where R₁ in the compound of formula I is hydrogen it is possible by appropriately selecting the conditions to alkylate that hydrogen atom and at the same time convert the product to a quaternary salt of general formula II.

The following Examples will serve to illustrate the invention:—

EXAMPLE 1.

(1:3 - Dimethyl - 2 - benzimidazole) (3¹ - methyl - 2¹ - benzothiazole) - 8 - methyl-8¹:9¹ - diazatri-methincyanine toluene - *p* - sulphonate.

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α - 1 - methyl - 2 - benzimidazolylethylidene) hydrazine (2.0 g.) was fused with methyl toluene - *p* - sulphonate (4.0 g.) at 150° for 2 hours. The mixture was cooled and lixivated with dry acetone to give a yellow solid which was filtered off and recrystallised from ethanol to give the pure dye as fine yellow needles, m.pt. 209—12°.

EXAMPLE 2.

(1 - Methyl - 2 - pyridine) (3¹ - methyl - 2¹ - benzothiazole) - 7 - methyl - 8¹:9¹ - diazatri-methincyanine toluene-*p*-sulphonate

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α -2-pyridylethylidene) hydrazine (2.0 g.) and methyl toluene-*p*-sulphonate (4.0 ml.) were fused at 150—160° for 2 hours. The resulting solid was washed with dry benzene, filtered off and recrystallised from ethanol to give the pure dye as small yellow needles, m.pt. 203—5°.

EXAMPLE 3.

(1 - Methyl - 4 - pyridine) (3¹ - methyl - 2¹ - benzothiazole) - 7 - methyl - 8¹:9¹ - diazatri-methincyanine toluene-*p*-sulphonate

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α -4-pyridylethylidene) hydrazine (2.0 g.) and methyl toluene-*p*-sulphonate (4.0 g.) were fused at 150—160° for 2 hours to give an orange solid. This solid was ground with dry

benzene and then recrystallised from ethanol to give the pure dye as orange needles, m.pt. 233°.

EXAMPLE 4.

(1 - Methyl - 2 - quinoline) (3¹ - ethyl - 2¹ - benzothiazole) - 9 - methyl - 8¹:9¹ - diazatri-methincyanine bromide

1 - (3 - Ethyl - 2 - benzothiazolinylidene)-2-(α -2-quinoly-lethylidene) hydrazine (2.5 g.) and methyl toluene-*p*-sulphonate (5.0 g.) were fused at 150° for 4 hours. The resulting orange melt was dissolved in ethanol and the solution was added to 25% aqueous sodium bromide (120 ml.) to give an orange solid. This solid was filtered off, ground with benzene and recrystallised from ethanol to give the pure dye as dark red needles, m.pt. 229°.

EXAMPLE 5.

Bis (3-methyl-2-benzothiazole) - 8 - methyl-8¹:9¹-diazatri-methincyanine bromide

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α -2-benzothiazolyl-ethylidene) hydrazine (1.55 g.) and methyl toluene-*p*-sulphonate (3.1 g.) were fused at 155—160° for 2 hours. The resulting deep red solid was ground with dry ether and then boiled out with acetone to give the crude dye toluene-*p*-sulphonate. This salt was dissolved in methanol (20 ml.) and added to 15% sodium bromide (20 ml.) to give a red solid which was filtered off and recrystallised from water to give the pure dye as orange-red needles, m.pt. 207°.

The following dyes were prepared from the bases of the co-pending Application referred to above by fusing with methyl toluene-*p*-sulphonate in the manner of Example 1.

EXAMPLE 6.

(3 - Methyl - 2 - benzothiazole) (1¹ - methyl-4¹ - pyridine) - 7¹ - phenyl - 8:9 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (3 - methyl - 2 - benzothiazolinylidene) - 2(α - 4 - pyridylbenzylidene) hydrazine and crystallised from ethanol as orange leaflets, m.pt. 214°.

EXAMPLE 7.

(3 - Methyl - 2 - benzothiazole) (1¹ - methyl-2 - quinoline) - 9¹ - benzyl - 8:9 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (3 - methyl - 2 - benzothiazolinylidene) - 2(α - 2 - quinolyl - β - phenylethylidene) hydrazine and crystallised from ethanol as red microcrystals, m.pt. 249—52°.

EXAMPLE 8.

(6 - Ethoxy - 3 - methyl - 2 - benzothiazole) (1¹ - methyl - 4¹ - pyridine) - 7¹ - methyl-8:9 - diazatri-methincyanine toluene - *p* - sulphonate was obtained from 1-(6-ethoxy-3-methyl-2-benzothiazolinylidene) - 2(α - 4 - pyridylethylidene) hydrazine and crystallised from ethanol as orange-red needles, m.pt. 241—3°.

EXAMPLE 9.

- (1 - Methyl - 2 - quinoline) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 9:10 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (1:2 - dihydro - 1 - methyl - 2 - quinolinylidene) - 2(α - 2 - benzothiazolylethylidene) hydrazine and crystallised from ethanol as orange-red needles, m.pt. 216°.

EXAMPLE 10.

- (6 - Methoxy - 3 - methyl - 2 - benzothiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 8:9 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (6 - methoxy - 3 - methyl - 2 - benzothiazolylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine and crystallised from ethanol as red plates, m.pt. 209—11°.

EXAMPLE 11.

- (5:6 - Dimethoxy - 3 - methyl - 2 - benzothiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 8:9 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (5:6 - dimethoxy - 3 - methyl - 2 - benzothiazolylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine and crystallised from ethanol as red plates with a green reflex, m.pt. 219—222°.

EXAMPLE 12.

- (3 - Methyl - 5 - methylthio - 2-1:3:4 - thiadiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 6:7 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1 - (3 - methyl - 5 - methylthio - 2 - Δ⁴-1:3:4 - thiadiazolylidene) - 2(α - 2 - benzothiazolylethylidene) hydrazine and crystallised from ethanol as light orange plates, m.pt. 203—6°.

EXAMPLE 13.

- (1 - Methyl - 2 - quinoline) (1¹ - ethyl - 4¹ - pyridine) 7¹ - phenyl - 9:10 - diazatri-methincyanine toluene-*p*-sulphonate. 1 - (1:2 - Dihydro - 1 - methyl - 2 - quinolinylidene) - 2 - (α - 4 - pyridylbenzylidene) hydrazine (1.0 g.) and ethyl toluene-*p*-sulphonate (2.0 g.) were fused together at 150° for 4 hours. Dry acetone (50 ml.) was added to the melt and the dye slowly crystallised out. The solid was filtered off and dried to give the product as small red plates, m.pt. 180—5°.

EXAMPLE 14.

- (3 - Methyl - 2 - benzothiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - ethyl - 8:9 - diazatri-methincyanine iodide was obtained from 1-(3-methyl-2-benzothiazolylidene)-2-(α - 2 - benzothiazolylethylidene) hydrazine by fusing with methyl toluene-*p*-sulphonate in the manner of Example 1, precipitated with potassium iodide in methanol and crystallised from methanol as red needles, m.pt. 243—4°.

EXAMPLE 15.

- (1 - Methyl - 2 - quinoline) (1¹ - benzyl - 4¹ - pyridine) - 7¹ - phenyl - 9:10 - diazatri-methincyanine bromide 1(1:2 - Dihydro - 1 - methyl - 2 - quinolinylidene) - 2(α - 4 - pyridylbenzylidene) hydrazine (1.0 g.), chloroform (10 ml.) and benzyl bromide (2 ml.) were boiled under reflux with a calcium chloride guard tube for 6 hours. Dilution with dry acetone slowly gave the product as orange-red plates, m.pt. 236—237° after filtration and drying.

EXAMPLE 16.

- (6 - Ethoxy - 3 - methyl - 2 - benzothiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 8:9 - diazatri-methincyanine methosulphate 1 - (6 - Ethoxy - 3 - methyl - 2 - benzothiazolylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine (1.0 g.) was dissolved in boiling dry benzene (20 ml.) and dimethyl sulphate (1.0 ml.) added. After boiling for 16 hours, a mass of dark crystals were present and were filtered off, washed well with benzene and purified by boiling out with acetone to give the pure dye as dark red needles, m.pt. 205—8°.

EXAMPLE 17.

- (3 - Methyl - 2 - benzothiazole) (1¹ - methyl - 4¹ - pyridine) - 7¹ - phenyl - 8:9 - diazatri-methincyanine methylsulphate was obtained by a method similar to that of Example 16 from 1 - (3 - methyl - 2 - benzothiazolylidene) - 2 - (α - 4 - pyridylbenzylidene) hydrazine and crystallised from ethanol as yellow needles, m.pt. 227°.

EXAMPLE 18.

- (1 - Methyl - 4 - quinoline) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 9:10 - diazatri-methincyanine toluene-*p*-sulphonate was obtained from 1(1:4-dihydro-1-methyl-4-quinolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine as bronze leaflets from water, m.pt. 215—8°.

EXAMPLE 19.

- (2 - Methyl - 6 - phenyl - 3 - pyridazine) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 7:8 - diazatri-methincyanine methosulphate was obtained from 1(2-methyl 2:3 - dihydro - 6 - phenyl - 3 - pyridazinylidene)2(α-2-benzothiazolylethylidene) hydrazine by a method similar to that of Example 16 and purified by boiling out with acetone to give the pure dye as red microcrystals, m.pt. 218°.

EXAMPLE 20.

- (5 - Chloro - 3 - methyl - 2 - benzothiazole) (3¹ - methyl - 2¹ - benzothiazole) - 8¹ - methyl - 8:9 - diazatri-methincyanine metho-

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- 5 sulphate was obtained from 1(5-chloro-3-methyl - 2 - benzothiazolinyldene) - 2(α - 2-benzothiazolyldene) hydrazine by a method similar to that of Example 16 and purified by boiling out with acetone to give the pure dye as red microneedles, m.pt. 264—66°.

EXAMPLE 21.

- 10 Bis (3 - Methyl - 2 - benzothiazole) - 8¹-methyl - 8:9 - diazatriethincyanine iodide
1 - (2 - Benzothiazolyl) - 2 - (α - 2 - benzothiazolyldene) hydrazine (2.5 g.), methyl iodide (5 ml.) and methanol (10 ml.) were
15 boiled under reflux for 40 hours. The mixture was cooled and the crystals filtered off. After washing with cold methanol the solid was extracted in a soxhlet apparatus with boiling
20 benzene to remove the last traces of the original base. The solid remaining was recrystallised from methanol to give the pure dye as small orange leaflets, m.pt. 194—6°.

EXAMPLE 22.

- 25 (3 - Methyl - 2 - benzothiazole) (1¹ - methyl - 2¹ - quinoline) - 9¹ - phenyl - 8:9 - diazatriethincyanine toluene-*p*-sulphonate
1(3 - Methyl - 2 - benzothiazolinyldene)-
2(α - 2 - quinolylbenzylidene) hydrazine (1.5 g.) and methyl toluene-*p*-sulphonate (3.0 g.)
30 were fused in an oil bath for 1 hour at 130° The melt was dissolved in dry acetone and allowed to stand. An orange crystalline mass

Dyeings of compound of Example 1 on
" " " " Example 2 "
" " " " Example 3 "
" " " " Example 22 "

- 65 The present invention accordingly includes the compounds of general formula II, their production by the methods described, the dyeing of textile materials, particularly polyacrylonitrile materials, by means of said com-

was present the next day and was filtered off and washed well with acetone to give the pure dye as red microcrystals, m.pt. 118°.

EXAMPLE 23.

This Example illustrates the dyeing of polyacrylonitrile fibres with the compounds of the present invention:—

0.5 Parts of the dyestuff obtained according to Example 5 are pasted with 0.5 parts of 80% acetic acid and dissolved by the addition of 4000 parts of hot water. A further part of 80% acetic acid, 2 parts of sodium acetate and 4 parts of a condensation product from olefin alcohol and 15 mols of ethylene oxide are added and 100 parts of polyacrylonitrile fibres are entered. The bath is heated to 90° within 30 minutes, kept at this temperature for 10 minutes and then dyeing is performed at the boil for 1 hour. The dye bath is almost completely exhausted. The dyed goods are then soaped for 15 minutes at 80° in 5000 parts of water with the addition of a sulphonated fatty acid condensation product, rinsed and dried. The polyacrylonitrile fibres are dyed in a pure orange shade which has excellent fastness to washing and light.

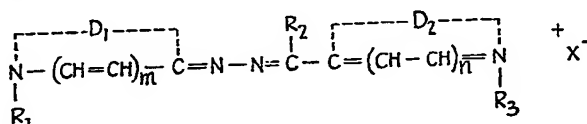
Preferred compounds for use in the dyeing of such fibres are those of Examples 1, 2, 3, 5 and 22, and, by using in a similar manner the dyes of these Examples, the following shades are obtained:—

polyacrylonitrile are greenish-yellow.
" " " " yellow.
" " " " orange-yellow.
" " " " orange.

pounds and the dyed materials so obtained.

WHAT WE CLAIM IS:—

1. Diazacarbocyanines of the general formula:—



- 75 wherein R₁ is an alkyl or aralkyl group, R₂ is an alkyl, aryl or aralkyl group, *m* and *n* are the same or different and are each nought or one, D₁ and D₂ are the same or different and are each a residue of a five-membered or six-membered heterocyclic nitrogen nucleus, R₃ is an alkyl or aralkyl group, and X is an anion.
80 2. Diazacarbocyanines according to claim 1 wherein R₁ is an alkyl group containing up to 4 carbon atoms.
3. Diazacarbocyanines according to claim 1 or 2 wherein R₂ is an alkyl group containing up to 4 carbon atoms, or a phenyl group.
85 4. (1:3 - Dimethyl - 2 - benzimidazole) (3¹-methyl - 2¹ - benzothiazole) - 8 - methyl-

8¹:9¹ - diazatriethincyanine toluene - *p*-sulphonate.

5. (1 - Methyl - 2 - pyridine) (3¹ - methyl - 2¹ - benzothiazole) - 7 - methyl - 8¹:9¹-diazatriethincyanine toluene - *p* - sulphonate.

6. (1 - Methyl - 4 - pyridine) (3¹ - methyl - 2¹ - benzothiazole) - 7 - methyl - 8¹:9¹-diazatriethincyanine toluene-*p*-sulphonate.

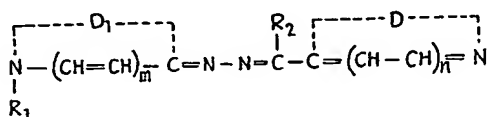
7. Bis (3 - methyl - 2 - benzothiazole) - 8-methyl-8¹:9¹-diazatriethincyanine bromide.

8. (3 - Methyl - 2 - benzothiazole) (1¹-methyl - 2¹ - quinoline) - 9¹ - phenyl - 8:9-diazatriethincyanine toluene-*p*-sulphonate.

9. A process for the production of a diazacarbocyanine as defined in claim 1 which com-

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prises reacting a compound of the general formula:—



5 where the symbols have the meanings assigned to them in claim 1, with a quaternising agent of the formula R_3X where the symbols have the meanings assigned to them in claim 1.

10 10. A process according to claim 9 wherein the reaction is effected by refluxing the reactants together.

11. A process according to claim 9 wherein the reaction is effected by fusing the reactants together.

15 12. A process for dyeing polymeric materials comprising at least 85% of acrylonitrile units

which comprises subjecting such materials to treatment with a solution in a dilute acid medium, or with a dispersion, of a diazocarbocyanine as defined in any of Claims 1—8.

13. Polymeric materials comprising at least 85% of acrylonitrile units dyed with a diazocarbocyanine as defined in any of claims 1—8.

14. A diazocarbocyanine according to claim 1 as specifically set forth in any one of the foregoing specific Examples 4 and 6—21 inclusive.

15. A process for the production of a diazocarbocyanine as defined in claim 1 substantially as set forth in any one of the foregoing specific Examples 1—22.

16. A process according to claim 12 substantially as set forth in the foregoing specific Example 23.

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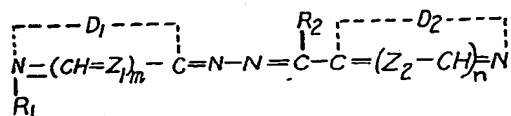
PROVISIONAL SPECIFICATION

Diazocarbocyanines

35 We, J. R. GEIGY S.A., a Swiss Company of Basle, Switzerland, do hereby declare this invention to be described in the following statement:—

This invention relates to new diazocarbocyanine dyes.

40 In our co-pending Application No. (Case A) there is described, *inter alia*, a new class of diazocarbocyanine bases of the general formula I:—



.....I

45 wherein R_1 is selected from alkyl, aryl, aralkyl, hydroxyalkyl and carboxyalkyl groups, R_2 is an alkyl, aryl or aralkyl group, Z_1 and Z_2 are the same or different and are each a methine ($-\text{CH}=\text{}$) group or a nitrogen atom, m and n are the same or different and are each nought or one, and D_1 and D_2 are the same or different and are each a residue of a five-membered or six-membered heterocyclic nitrogen nucleus. It is to be understood that the heterocyclic

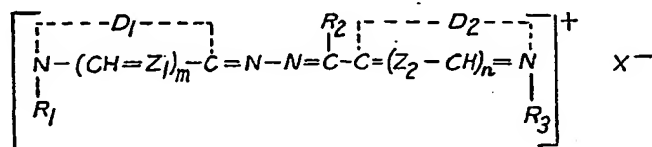
55 nuclei may be polynuclear, the additional rings

being themselves heterocyclic or isocyclic. Thus each may contain a fused benzene ring as, for example, in a quinoline nucleus. Phenyl groups and fused isocyclic or heterocyclic groups present in the compounds may themselves carry substituent groupings, e.g. alkyl, aryl, alkoxy, hydroxy, amino or acylamino groups or halogen atoms (e.g. chlorine or bromine).

60 Examples of heterocyclic nuclei of which D_1 and D_2 may be the residue are oxazole, thiazole, selenazole, pyridine, pyrrolidine, glyoxaline, pyrimidine, pyrazole, thiadiazole, triazole and their partially reduced derivatives (e.g. thiazoline) and the polynuclear derivatives of these such as benzothiazole, quinoline, indolenine, benzimidazole and quinazoline. Where the residues D_1 and D_2 include tertiary nitrogen atoms of the form $-\text{NR}^1-$, R^1 may be hydrogen, alkyl, aryl or aralkyl.

75 The group R_1 may be an alkyl or hydroxyalkyl group containing up to 4 carbon atoms and the group R_2 may be an alkyl group containing up to 4 carbon atoms or a phenyl group.

80 According to the present invention there are provided quaternary ammonium salts of the said compounds of formula I, being compounds of the general formula II:—



.....II

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where the symbols R_1 , R_2 , D_1 , D_2 , Z_1 , Z_2 , m and n have the meanings assigned to them above, R_3 is an alkyl, aralkyl, hydroxyalkyl, carboxyalkyl or aryl group and X is the anion of an acid, e.g. toluene-*p*-sulphonate, halide (chloride, bromide or iodide), sulphate, methosulphate, perchlorate or sulphamate.

Preferably the said compounds are prepared by treating a compound of general formula I with a quaternising agent of the formula R_3X , e.g. by refluxing with or without an inert solvent, if R_3X is of suitable volatility, or by fusing the reactants at elevated temperature.

The resulting dyes are valuable dyestuffs for polymeric materials consisting essentially of polymers of acrylonitrile and copolymers of acrylonitrile with other monomeric materials. Generally the polymers will contain at least 85 per cent of acrylonitrile units and a particular commercial material of the type, essentially in the form of textile fabric, is sold under the trade name ORLON. Such polymers are difficult to dye by the use of conventional dyestuffs and the compounds of the present invention provide a new class of dyestuff of exceptional value in the dyeing of such materials. The dyeing is preferably effected in a dilute acid medium.

The dyes of formula II may be rendered of suitable solubility by treating with an aqueous solution of a salt MY where M is ammonium or an atom of an alkali metal (e.g. sodium or potassium) and Y is an anion, e.g. any of those referred to in connection with X whereby the radicle X is replaced by the radicle Y so that the solubility of the product is varied. Where R_1 in the compound of formula I is hydrogen it is possible by appropriately selecting the conditions to alkylate that hydrogen atom and at the same time convert the product to a quaternary salt of general formula II.

The following Examples will serve to illustrate the invention:—

EXAMPLE 1.

(1:3 - Dimethyl - 2 - benzimidazole) (3^1 -methyl - 2^1 - benzothiazole) - 8 - methyl- 2^1 : 9^1 - diazatri-methincyanine toluene - *p*-sulphonate.

1 - (3 - Methyl - 2 - benzothiazolinyldene)-2-(α -1-methyl - 2 - benzimidazolylethylidene) hydrazine (2.0 g.) (Example 2 of our copending application) was fused with methyl toluene-*p*-sulphonate (4.0 g.) at 150° for 2 hours. The mixture was cooled and lixiviated with dry acetone to give a yellow solid which was filtered off and recrystallised from ethanol to give the pure dye as fine yellow needles, m.pt. $209-12^\circ$.

EXAMPLE 2.

(1 - Methyl - 2 - pyridyl) (3^1 - methyl - 2^1 -benzothiazolyl) - 7 - methyl - 8^1 : 9^1 -diazatri-methincyanine toluene-*p*-sulphonate.

trimethincyanine toluene-*p*-sulphonate.

1 - (3 - Methyl - 2 - benzothiazolinyldene)-2-(α -2-pyridyl-ethylidene) hydrazine (2.0 g.) (Example 3 of our co-pending application) and methyl toluene-*p*-sulphonate (4.0 ml.) was fused at $150-160^\circ$ for 2 hours. The resulting solid was washed with dry benzene, filtered off and recrystallised from ethanol to give the pure dye as small yellow needles, m.pt. $203-5^\circ$.

EXAMPLE 3.

(1 - Methyl - 4 - pyridyl) (3^1 - methyl - 2^1 -benzothiazole) - 7 - methyl - 8^1 : 9^1 - diazatri-methincyanine toluene-*p*-sulphonate.

1 - (3 - Methyl - 2 - benzothiazolinyldene)-2-(α -4-pyridylethylidene) hydrazine (2.0 g.) (Example 4 of our co-pending application) and methyl toluene-*p*-sulphonate (4.0 g.) were fused at $150-160^\circ$ for 2 hours to give an orange solid. This solid was ground with dry benzene and then recrystallised from ethanol to give the pure dye as orange needles, m.pt. 233° .

EXAMPLE 4.

(1 - Methyl - 2 - quinoline) (3^1 - ethyl - 2^1 -benzothiazole) - 9 - methyl - 8^1 : 9^1 - diazatri-methincyanine bromide.

1 - (3 - Ethyl - 2 - benzothiazolinyldene)-2-(α - 2 - quinolyethylidene) hydrazine (Example 5 of our co-pending application) (2.5 g.) and methyl toluene-*p*-sulphonate (5.0 g.) were fused at 150° for 4 hours. The resulting orange melt was dissolved in ethanol and the solution was added to 25% aqueous sodium bromide (120 ml.) to give an orange solid. This solid was filtered off, ground with benzene and recrystallised from ethanol to give the pure dye as dark red needles, m.pt. 229° .

EXAMPLE 5.

Bis (3 - methyl - 2 - benzothiazole) - 8-methyl- 8^1 : 9^1 -diazatri-methincyanine bromide.

1 - (3 - Methyl - 2 - benzothiazolinyldene)-2-(α -2-benzothiazolylethylidene) hydrazine (1.55 g.) (Example 9 of our copending application) and methyl toluene-*p*-sulphonate (3.1 g.) were fused at $155-160^\circ$ for 2 hours. The resulting deep red solid was ground with dry ether and then boiled out with acetone to give the crude dye toluene-*p*-sulphonate. This salt was dissolved in methanol (20 ml.) and added to 15% sodium bromide (20 ml.) to give a red solid which was filtered off and recrystallised from water to give the pure dye as orange-red needles, m.pt. 207° .

The present invention accordingly includes the compounds of general formula II, their production by the method described, the dyeing of textile materials, particularly polyacrylonitrile materials, by means of said compounds and the dyed materials so obtained.

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